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# Pressure induced spin-crossover in $\text{EuFeO}_3$

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$\text{EuFeO}_3$  perovskite has been studied by using  $^{57}\text{Fe}$  Mössbauer effect and X-ray diffraction under pressures up to 90 GPa and in the temperature range of 4.2-300 K. A high-pressure-induced first order phase transition is observed in the pressure range of 45 - 52 GPa as manifested by a discontinuous volume and IS reduction and dramatic changes of the hyperfine interaction parameters. The high-pressure phase of  $\text{Fe}^{3+}$  is established as a *low-spin* state ( $S=1/2$ ,  $^2T_{2g}$ ) characterized by spin-spin magnetic relaxation spectra to the lowest temperature. The nature and mechanism of the magnetic relaxation are discussed.

## 1. Introduction

As a result of a breakdown of Hund's rule at very high density of matter, the high spin (HS) state of transition metal compounds may convert to a low spin (LS) state at some high enough pressure. The availability of very high-pressure (HP) diamond anvil cells (DAC) combined with appropriate spectroscopic methods has allowed us to study this rather fundamental property in solid state physics [1-2].

To date orthoferrite  $R\text{FeO}_3$  ( $R=\text{La, Pr}$ ) is the only *trivalent* iron system in which a HP induced spin-crossover has been directly observed [3-4]. In  $\text{Fe}^{3+}$  compounds ( $d^5$ ), the electronic configu-

ration of the HS and LS states are  $(t_{2g}^* \uparrow)^3 (e_g^* \uparrow)^2$  and  $(t_{2g}^* \uparrow)^3 (t_{2g}^* \downarrow)^2$ , respectively. Mössbauer spectroscopy is undoubtedly the best and probably the only spectroscopic method for studying the electronic ground state of these systems at very high pressures.

In the present work,  $\text{EuFeO}_3$  perovskite has been studied by using  $^{57}\text{Fe}$  Mössbauer effect and X-ray diffraction under pressures up to 90 GPa and in the temperature range of 4.2-300 K.

## 2. Experimental

The sample was prepared in vacuum by direct solid-solid reaction of stoichiometric mixture of  $\text{EuO}_2$  and  $\text{Fe}_2\text{O}_3$  powder at high temperature, the latter enriched to 20%  $^{57}\text{Fe}$ . The Tel-Aviv miniature piston/cylinder DAC [5] was used with anvils having 400- or 200- $\mu\text{m}$  diameter culet size for the pressure range of 2 - 60 GPa and 60 – 90 GPa, respectively. Samples were contained in 200- or 100- $\mu\text{m}$  cavities drilled in a Re gasket that also served as a collimator for the 14.4-keV  $\gamma$ -rays. Argon was used as a pressurizing medium and ruby fluorescence served as a manometer. Mössbauer studies were carried out with a  $^{57}\text{Co}(\text{Rh})$  10 mCi point source in the 4 – 300 K temperature range using a top-loading LHe cryostat. All spectra were analyzed using appropriate MS fitting programs from which the hyperfine interaction parameters and the respective abundance of spectral components were derived. X-ray diffraction measurements with synchrotron radiation were carried out at 300 K in the angle dispersive mode using the monochromatic beam of the ID30 station at the European Synchrotron Radiation Facilities (ESRF).

## 3. Results

The room temperature pressure evolution of the Mössbauer spectra is shown in Fig. 1. Spectrum at ambient pressure can be well fitted with a single sextet, and the hyperfine field ( $H_{\text{hf}}$ ) is 51

T. In the pressure range of 42 – 52 GPa a new nonmagnetic component emerges in the central region of the spectrum. The Equation of State based on preliminary XRD data reveals a ~4% volume contraction near 45 GPa (Fig. 2c) [6]. The relative abundance of the magnetic component has been calculated from the absorption areas in each sub-spectrum and is depicted in Fig. 2a. The IS data pertaining to the low-pressure (LP) (○) and HP (●) phases are shown in Fig. 2b in which an abrupt drop of the IS (an abrupt increase in  $\rho_s(0)$ ) is observed, in accordance with the volume contraction at the phase transition.

At  $P > 50$  GPa, only the HP phase is present. The temperature dependence of the Mössbauer spectra at 54 GPa is shown in Fig. 3. Starting at 300 K the quadruple splitting (QS) is 0.55 mm/s, increases to 0.99 mm/s at 100K. Near 90 K the onset of a magnetic splitting appears. Below 50 K the general spectra shape does not change any more. This shape is characteristic of magnetic relaxation and its origin is the onset the LS  $\text{Fe}^{3+}$  state ( $S = 1/2$ ,  $^2T_{2g}$ ). The fit shown (solid curve) was carried out using the formalism developed for  $^{166}\text{Er}$  MS in  $\text{ErFeO}_3$  by Nowik and Wickman [7]. This relatively simple theoretical formalism assumes a system of two spin-state manifolds. They will mutually exchange energy between the  $S = -1/2$  and  $S = 1/2$  states within a characteristic relaxation time  $\tau$  akin to the  $^{57}\text{Fe}$  14.4 keV level lifetime. The probabilities of the system to be in spin up and down states are given by  $p_B$  and  $p_A$ , respectively with  $p_A + p_B = 1$ .  $H_{\text{hf}}$  obtained by fitting the 10 K spectrum is ~30 T. The typical relaxation time is 5.9 ns, independent of temperature. For 54 GPa  $p_A = 0.18$  and barely changes with pressure. The QS increases with pressure, reaching 0.92 mm/s at 91 GPa at 300 K.

#### 4. Discussion and Conclusions

The temperature dependence of the QS is a major manifestation of the HP phase, LS-state. It has a single unpaired spin thus providing the major contribution to the large electric field gradient. It shows an appreciable thermal population of the close-lying excited electronic levels contrary to the HS state, which is temperature independent. The unpaired spin also produces a significant orbital contribution to  $H_{hf}$ , leading to its relatively large value of 30 T compared to the spin only term, which is  $\sim 11$  T.

The fact that the relaxation time is independent of temperature implies that the nature of the magnetic relaxation is spin-spin relaxation (inter-atom exchange of  $S_Z$  values). A nominal  $^2T_{2g}$  ground state arising from the  $t^5_{2g}$  configuration of LS  $d^5$  ( $Fe^{3+}$ ) can suffer the lifting of its sixfold degeneracy via a combination of spin-orbital splitting effects and low-symmetry ligand field components. Therefore the spin-up and spin-down states may have a slight energy difference. The energy used for the spin flip must be taken from the magnetic dipolar energy of the whole system, resulting in the spin-spin relaxation. When the possibility of the electron at a certain spin state is larger than the other one, a partial magnetic order would be observed.

In  $LaFeO_3$  and  $PrFeO_3$ , at the structural phase transition, two spin sub-lattices are formed with equal abundance, one LS and the other remaining in the HS state. The ultimate pure LS state is reached only after a further 10 GPa increase [4]. In  $EuFeO_3$  the spin-crossover is 100% concurrent with the structural phase transition despite the very similar size of the volume collapse. This phenomena can be understood on the basis of the intrinsically smaller atomic radius of Eu at ambient pressure, resulting in an additional distortion of the  $FeO_6$  octahedron, consequently, a larger crystal field energy compared to the La and Pr. We are now investigating the HP properties of the smaller radii  $R$ -ions orthoferrites to further elucidate the spin-crossover mechanism of the ferric ions at HP.

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**Figure Captions:**

Figure 1. Room temperature Mössbauer spectra of  $\text{EuFeO}_3$  in the pressure range of 6 - 52 GPa. The solid curve represents the theoretical fit. Dashed and dotted curves represent, respectively, the LP and HP phase in the coexistence regions.

Figure 2. (a) Pressure dependence of the HP phase abundance, (b) pressure dependence of the IS, with respect to Fe metal at RT, and (c), the pressure evolution of the unit cell volume at room temperature. In the lower two figures ○ and ● correspond to the LP and HP phases, respectively.

Figure 3. Mössbauer spectra recorded at 54 GPa. Dotted and dashed curves represent, respectively, the paramagnetic and magnetic relaxation components, which coexist around the magnetic ordering temperature.

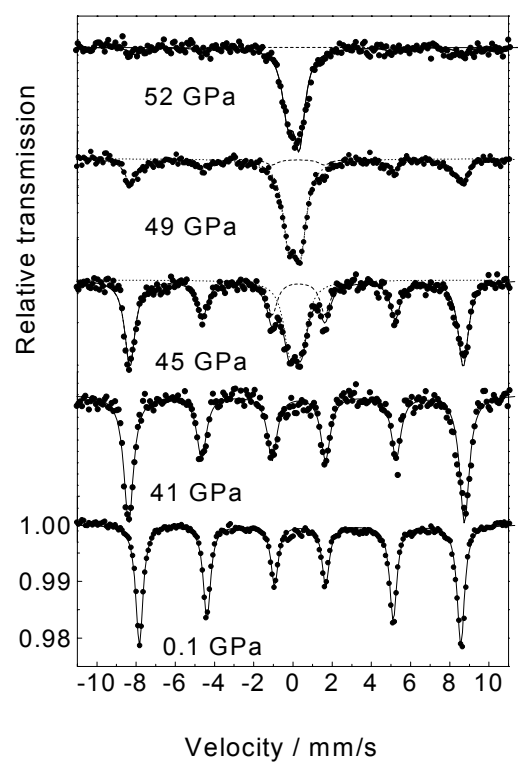


Fig.1 Xu et al.....

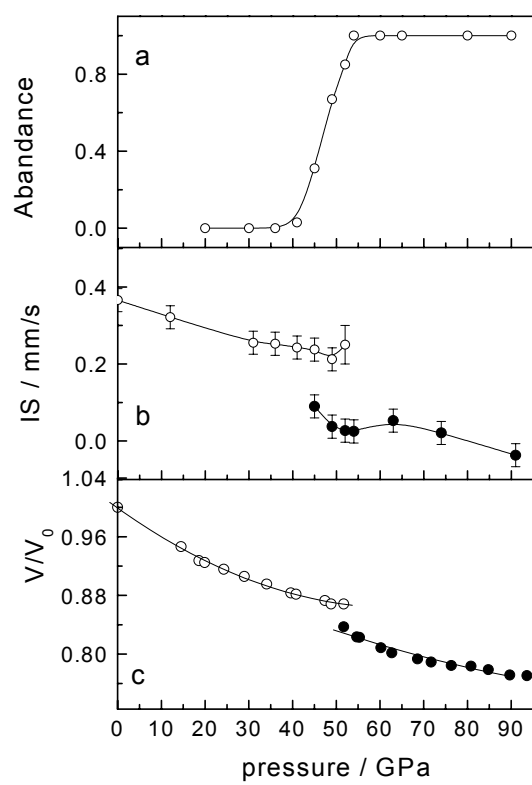


Fig. 2 Xu et al .....



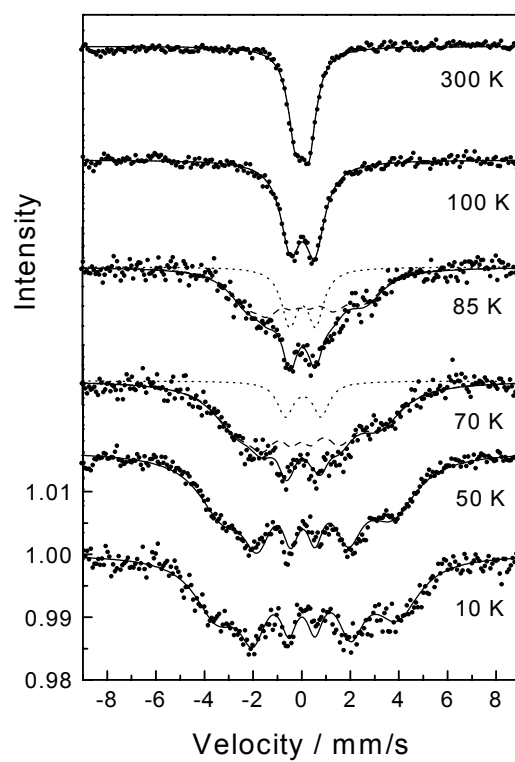


Fig. 3 Xu et al .....

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